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**A Colorimetric Estimation of the
Degree of Photochemical Degradation
of Polypropylene Films**

by

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A COLORIMETRIC ESTIMATION OF THE DEGREE OF PHOTOCHEMICAL DEGRADATION OF POLYPROPYLENE FILMS

by A.P.B. MAASDORP and WENDY A. BLACK

ABSTRACT

The photochemical degradation of unpigmented and unstabilised polypropylene films can be monitored colorimetrically following reaction of the carbonyl groups produced, with 2,4-dinitrophenylhydrazine under acidic conditions. The highly coloured 2,4-dinitrophenylhydrazone produced in the polymer films can be measured either on a tristimulus colorimeter (ΔE) or by UV/visible spectrophotometry at 340 nm. The degradative progress could also be seen fairly easily by examination of the irradiated polypropylene films under a scanning electron microscope.

INTRODUCTION

The photodegradation of polypropylene, during exposure to sunlight, is a serious problem in the industry, affecting, *inter alia*, the strength of the textile products which are made from it, but to date, a quick and inexpensive method of assessing the degree of degradation has not been found.

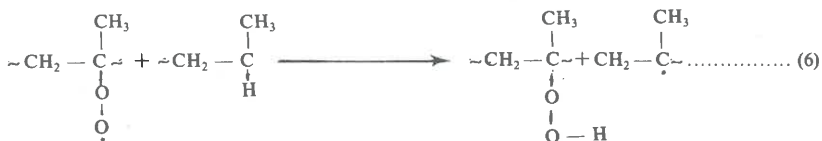
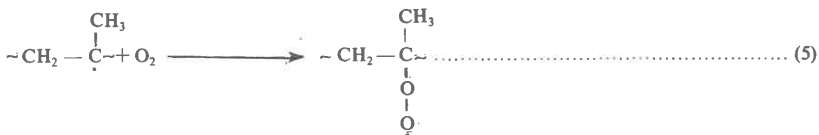
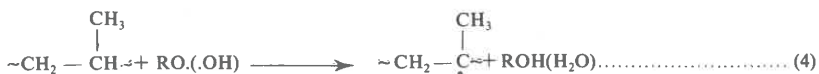
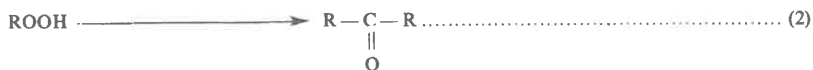
Owing to its paraffinic hydrocarbon nature, polypropylene should be transparent to ultraviolet (U.V.) light and not absorb energy in the region of 200 to 400 nm. The high molecular weight polypropylene macromolecule in reality is sensitive to U.V. light and the formation of degradation products indicates the presence of sensitive centres, hydroperoxides and ketones (impurities) in the polymer in trace quantities. These impurities are present either initially or formed during the polymer extrusion process^{1, 2, 3}. The hydroperoxides and ketones therefore initiate the photo-oxidation of polypropylene, absorbing the U.V. light in the region 310 to 330 nm².

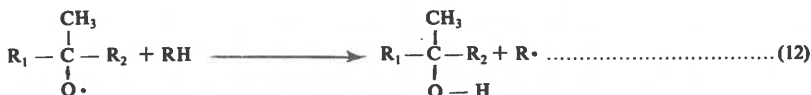
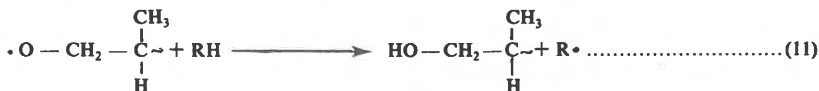
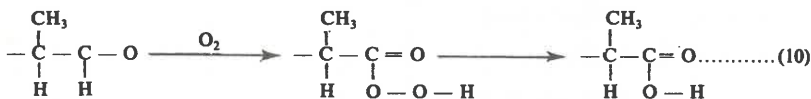
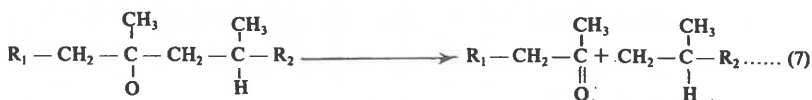
Balaban *et al*³ have proposed a mechanism for the photodegradation of polypropylene [equations (1) to (12)]. A short outline of the scheme follows:

Catalytic impurities (trace quantities) in the polypropylene react with oxygen to form hydroperoxides [eq. (1)] which eventually further form carbonyl compounds [eq. (2)]. The hydroperoxidic groups are subsequently photolytically cleaved according to eq. (3). This is regarded as the most important initiation reaction, promoting the photo-oxidation process by producing kinetically unstable free radicals amongst the polymer chains. A hydrogen atom may then be split off from a tertiary carbon by one of these free radicals according to eq. (4). The free radical formed on the tertiary carbon atom

then reacts with oxygen producing a peroxy radical [eq. (5)]. The latter peroxy radical, upon reaction with a monomeric unit produces a hydroperoxidic group and a free radical [eq. (6)]. The free radical produced can once again react with oxygen [eq. (5)] and split according to eq. (3). The next step in the photochemical degradation mechanism is the formation of carbonyl groups in the polymer. Eq. (7) is an assumed mechanism. A carbonyl group and a double bond can also be formed, should there be isomerisation of the bi-radical [eq. (8)]. Carbonyl groups may, besides forming at the end of a macro-molecule, also form on the backbone of the polymeric chain [eq. (9)]. However, eq. (7) is considered the most likely for the formation of carbonyl groups, since it depicts the decrease in molecular weight of the polymer by chain breaking. Furthermore, eq. (8) is less likely since an accumulation of double bonds in the polymer has not been found. Apparently, aldehydic groups are also formed and subsequently oxidised to carboxylic acids [eq. (10)]. Finally, there are the hydroxyl groups formed at the end of a macromolecule [eq. (11)] or in the middle of a macromolecule [eq. (12)] through reaction of a cleaved hydroperoxide (RO.) with the polymer.

Photochemical Degradation of Polypropylene — Mechanism proposed by Balaban, Majer and Vesely³





Polypropylene, although susceptible to the photochemical degradation sequences shown, has excellent resistance to chemicals, desirable physical properties and is generally recognised to be a useful and low priced polymer in a variety of applications¹. Depending on the intended use of the fibre, the light stability requirements for polypropylene vary considerably. For outdoor applications, the best attainable fibre stability is needed, whereas for apparel the requirements are relatively low.

It is therefore of primary importance not only to prevent this photochemical degradation of polypropylene but also to monitor its progress in the polymer. Generally, four basic types of stabiliser are used to prevent the photochemical reactions of the hydroperoxides and ketones in polypropylene^{1, 2}. They are:

1. Antioxidants — to prevent the thermal degradation often occurring simultaneously with photodegradation. They contribute least to light stabilization of polypropylene.

2. U.V. screeners — absorb U.V. light. Most commonly used.
3. Peroxide decomposers — deactivate the hydroperoxides and so prevent the formation of radicals.
4. Energy quenchers — to quench the excited states of the ketonic groups.

The progress of photodegradation manifests itself in a number of chemical and physical ways⁴. These are:

1. Change in molecular weight
2. Change in colour (yellowing or fading)
3. Formation of surface cracks
4. Loss of surface gloss
5. Reduction of flex resistance
6. Reduction of tensile strength
7. Reduction of impact resistance.

A measure which permits practical testing of the photochemical degradation progress is the time necessary for the tensile strength to decrease to 50% of its initial value⁴. The degradation of polypropylene also results in a large build up of oxidation products, i.e. hydroperoxides, carbonyls and hydroxy groups^{3,5}. These can be monitored by infra red spectroscopy at 3400 cm^{-1} (hydroxy and hydroperoxy groups) and at 1715 cm^{-1} (carbonyl groups). Hydroperoxy (-OOH) levels can also be monitored by iodometric titration after solution and precipitation⁶.

For the purposes of this study, it was decided to develop an alternative quick and simple means of assessing photodegradation of polypropylene.

EXPERIMENTAL

Samples

The present study was limited to unpigmented unstabilised polypropylene film (1 mm thickness). Circular samples (25 mm diameter) were cut out with the aid of a die and prepared for irradiation.

Method

2,4-Dinitrophenylhydrazine (0,4 gram) was dissolved in concentrated

sulphuric acid (2 ml). Water (3 ml) was added dropwise with shaking so warming the 2,4-dinitrophenylhydrazine/acid solution. The solution was further treated with alcohol (95%, 10 ml) whereupon the polypropylene film ($\pm 0,5$ gram) was added together with another alcohol addition (95%, 10 ml). The solution containing the polypropylene was refluxed for 1 hour. The polypropylene film was then removed, washed with water, air dried and soxhlet extracted (20 cycles) with ethyl acetate.

Apparatus

A Hanovia Model 500/A Ultra Violet lamp was used for irradiating the polypropylene films at a distance of 46 cm and at 25°C (sample temperature).

Colour difference values (ΔE) between unirradiated and irradiated 2,4-dinitrophenylhydrazine treated polypropylene films were measured on a Hunter Laboratory Tristimulus Colorimeter.

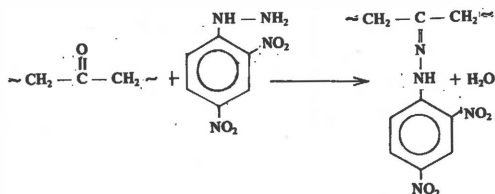
2,4 Dinitrophenylhydrazone absorption in the polypropylene films was determined at 340 nm on a Beckman UV/Visible Spectrophotometer.

The irradiated polypropylene films were also examined under the Scanning electron microscope (following gold coating) at a magnification of 400x and 15 kV accelerating potential.

RESULTS AND DISCUSSION

It is known that the weathering of unstabilised polypropylene causes a build up of hydroperoxide [eq. (6)] and carbonyl [eq. (7), (8) and (9)] groups in the polymer after a relatively short period of time. This oxidation product build-up has been monitored by infra-red spectroscopy at 3400 cm^{-1} (predominantly hydroperoxides) and 1715 cm^{-1} (carbonyl products)⁵.

While the hydroperoxide levels have been successfully measured chemically by iodometric titration⁶, little has been attempted in the way of chemically measuring the build up of carbonyl products in the polymer. For the purposes of the present investigation it was decided to use the known reaction of 2,4-dinitrophenylhydrazine with carbonyl groups under acidic conditions⁷ in order to monitor the photo-degradation of unstabilised, unpigmented polypropylene film. The general reaction scheme is as follows:



The highly coloured (yellow-red) 2,4-dinitrophenylhydrazine readily reacted under acidic conditions with the carbonyl groups produced in the polypropylene film as a result of photodegradation and formed the 2,4-dinitrophenylhydrazone (yellow). Unreacted 2,4-dinitrophenylhydrazine was rinsed away (soxhlet extraction with ethyl acetate) after the treatment and only the chemically bound hydrazone remained on the film. The increase in colour of the polypropylene film with increase in irradiated time is clearly visible and can be seen in Figure 1. To assess accurately the degree of yellow colouration it was decided to carry out colour measurements on a tristimulus colorimeter. The colour difference values (ΔE) between the irradiated samples and an unirradiated sample as reference or standard were calculated and are shown in Figure 2 as a function of irradiation time. Figure 2 shows an initial fast increase in colour difference up to about 35 hours irradiation whereupon the colour difference remains fairly stable. Alternatively, the yellow colouration of the polypropylene films was also measured by absorption in the visible region at 340 nm using an unirradiated polypropylene film as reference. The 2,4-dinitrophenylhydrazones are known to absorb in this region⁷. Figure 3, similar to Figure 2, shows an initial fast increase in absorption, whereupon the curve tends to level off.

Both methods show clearly that there is an initial fast build up of carbonyl products in the polypropylene film upon irradiation (up to 35 hours). Thereafter, the carbonyl level, as the level of 2,4-dinitrophenylhydrazone formation seemed to stay constant. One possible explanation for this steady state that is attained is that there is a progressive reduction in the polymer chain length on the surface of the films during exposure, and a loss of the shorter chains containing some hydrazone (yellow colouration) during the rinsing process (ethyl acetate extraction) due to solubilization. Due to the degradation of the primary irradiated surface to such an extent, it was felt that a second surface is exposed just underneath the first where once again the oxidation products form. This loss of primary irradiated surface colour and re-establishment of colour in the secondary layer therefore constitutes the steady state.

This assumption was confirmed by carefully preparing and mounting the irradiated 2,4-dinitrophenylhydrazine treated polypropylene film (with suitable gold coating) and examining such under a scanning electron microscope. The micrographs can be seen in Figure 4, arranged in increasing order of irradiation time. It is clear that within 8 hours the first cracks have formed in the polymer surface. The first major faults (cracks) appear after ± 30 hours and by 40 hours the surface is grossly damaged. By 80 hours the primary surface layers have begun to be removed. Irradiation has obviously also taken place underneath. Although this study of the photodegradation of the surface of the polypropylene film by scanning electron microscopy has only been of a confirmative nature, it is

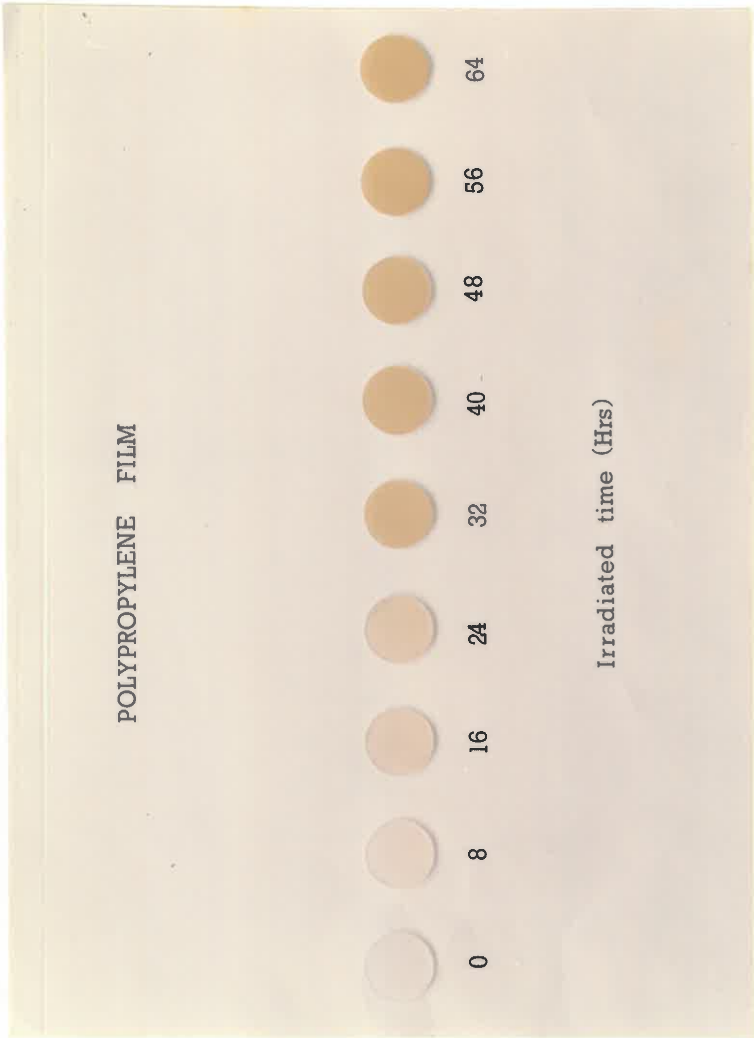


Figure 1 - The effect of exposure to ultra violet light on the colour of polypropylene film subsequently treated with acid 2,4-dinitrophenylhydrazine

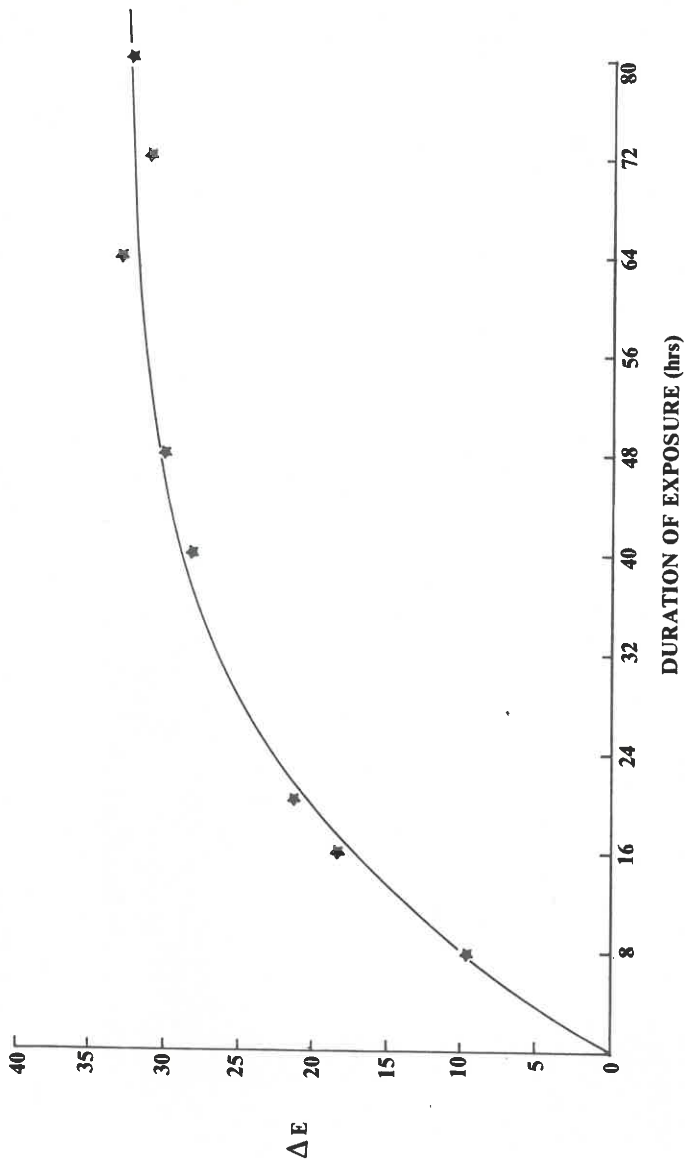


Figure 2 - The effect of duration of exposure on the colour difference values

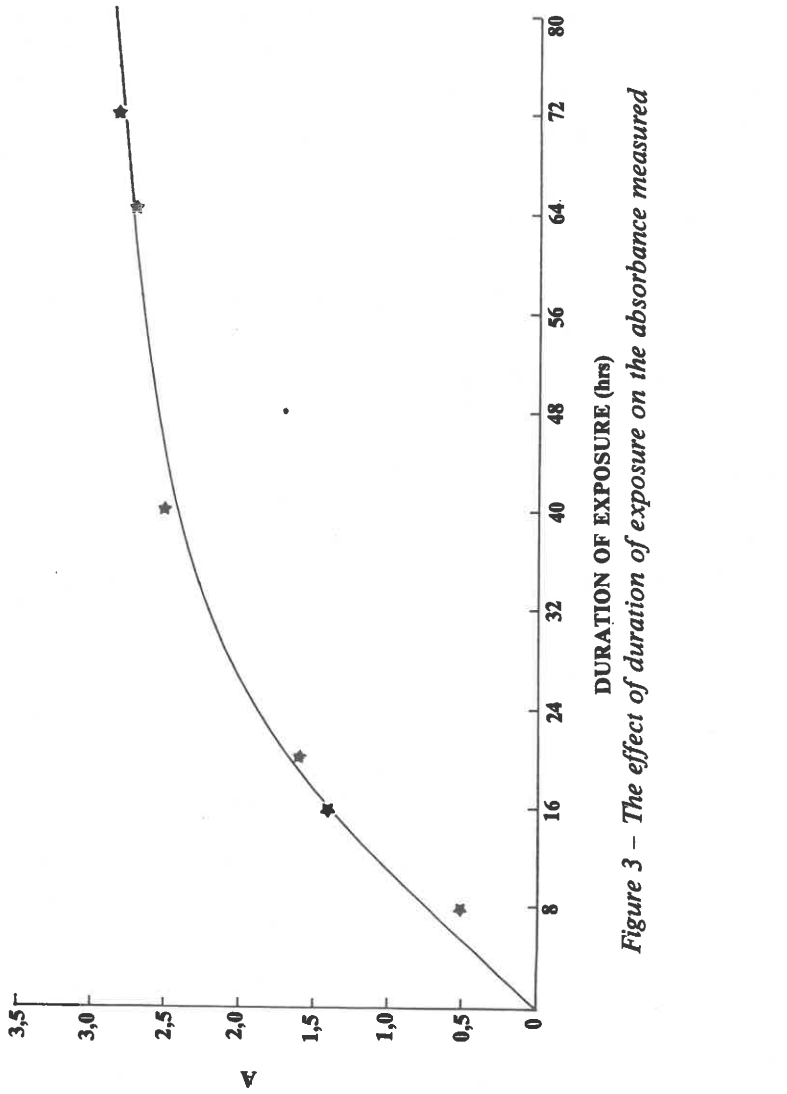
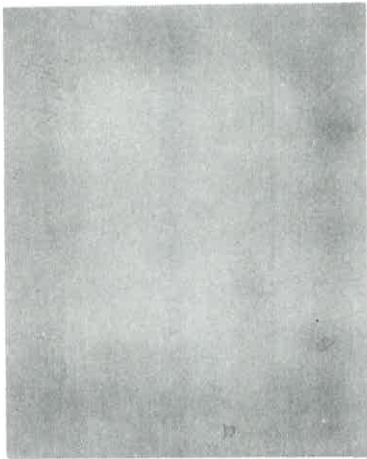
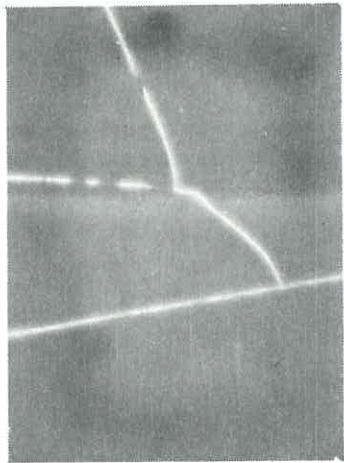


Figure 3 – The effect of duration of exposure on the absorbance measured



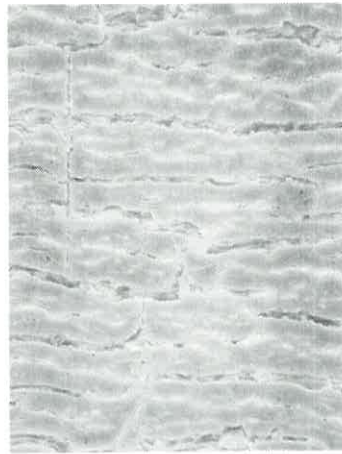
0 hrs



8 hrs

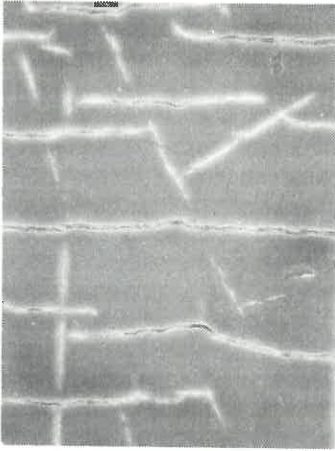


40 hrs

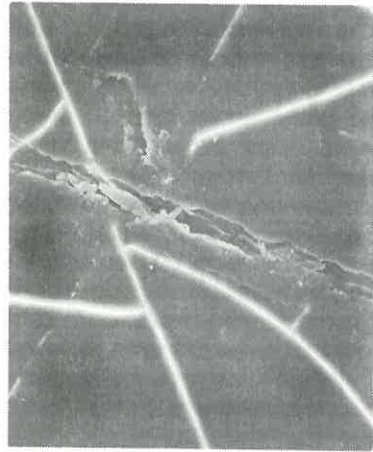


48 hrs

Figure 4 - Scanning Electron Micrographs (x 400) of polypropylene film subjected to increasing amounts of irradiation



16 hrs



24 hrs



64 hrs



80 hrs

possible that the scanning electron microscope could be used to also assist in assessing polymer fibre degradation. This method would, however, still need a lot of refining.

SUMMARY AND CONCLUSIONS

The build up of oxidation products, in particular carbonyl groups, in unstabilised and unpigmented polypropylene film following photodegradation, was measured by treating the exposed film with acidic 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones. Colour intensity can be measured either by means of colourimetry (ΔE) or by absorption spectroscopy (visible region, 340 nm). Scanning electron micrographs lend support to these findings and may in itself be a useful tool for rapidly assessing photodegradation. However, the use of 2,4-dinitrophenylhydrazine is an extremely simple and quick method for assessing the degree of photochemical degradation in polypropylene films. This work is being extended to cover pigmented and stabilised polypropylene products and their stability to natural U.V. radiation.

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REFERENCES

1. Bonkowski, J.E., *Textile Research Journal*, **39**, 243 (1969).
2. Olivieri, P., *Neueste Entwicklungen der Polypropylenfaser für Teppiche und Wandbekleidung*, Montefibre S.P.A. Milano, Intercarpet 75.
3. Balaban, L., Majer, J., Vesely, J. *Polymer Sci., Part C*, No. 22, 1059 (1969).
4. Berger, K., *Natural and artificial exposure and weathering of plastics*, Ciba Geigy A.G., Basle.
5. Carlsson, D.J., Garton, A., Wiles, D.M., *Adv. Chem. Serv.*, 169 (Stab. Degradation Polym.), 56-67 (1978).
6. Carlsson, D.J., Wiles, D.M., *Macromolecules*, **2**, 597 (1969).
7. Schütze, G., *Polymeranalytik und Austrüsten an Polypropylenfasern Photooxidative Abbauseruche an Polypropylen*, Dissertation for Ph D, RWTH, Aachen (1977).

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